Scientific Review
ISSN(e): 2412-2599, ISSN(p): 2413-8835
Vol. 3, No. 3, pp: 17-28, 2017
URL: http://arpgweb.com/?ic=journal&journal=10&info=aims

Interaction of Components in Molecular Optoelectronics for the Next Generation of IT Devices

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Abstract: The interaction of molecular optoelectronic components on the molecular scale were studied where the solvent shell indicating the influence of the medium was found to be surprisingly small. The transport of energy as resonant energy transfer covers distances of about 5 nm and was shown not to proceed by a simple to dipole dipole interaction with typical restrictions, but by a more complex mechanism. Furthermore, a novel-type of far-reaching interactions of electronically excited structures until macroscopic dimensions were fond and may be applied for addressing molecular structures by conventional electronics.

Keywords: Molecular optoelectronics; Energy transfer; FRET; Molecular addressing; Solvent shell; Medium effects.

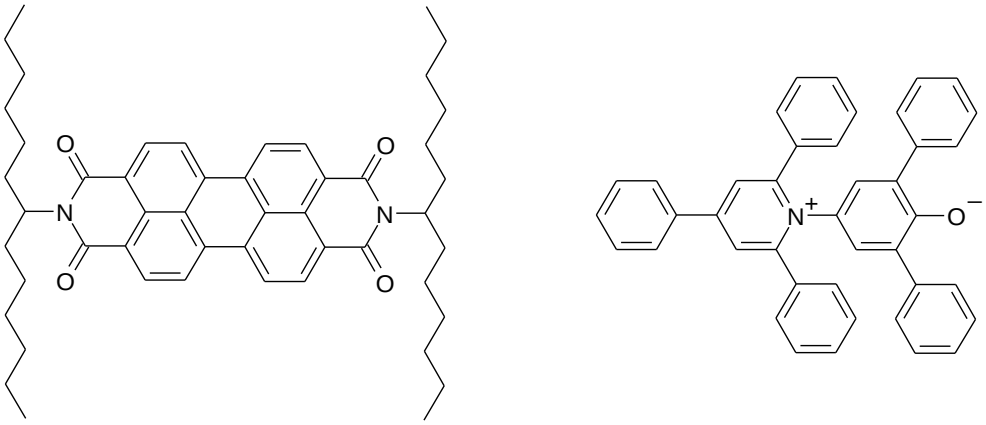
1. Introduction

Modern IT technology is targeted both to increasing integration with smaller getting components and increasing the speed of operation Hilbert and López [1]. Tendencies for the preference of molecular optical technologies for the next generation of devices are obvious Carroll and Gorman [2]. Optical technologies are attractive because the frequencies of operation may reach petahertz region just below the limit of uncontrolled ionization of basic chemical structures causing damage of materials Langhals [3]. Moreover, a manifold of optical functional chemical structures required for the construction of complex arrangements have already been developed. However, the small molecular dimensions of such units seem to be dominated by quantum effects ruling out many convenient concepts. One may demand how far the present macroscopic electronic technology (determined by the physics of macroscopic things) is still valid for microscopic (molecular) devices and how far quantum mechanics may become important. The exact prediction of the behavior of macroscopic arrangement on the basis of the knowledge of microscopic molecular properties and vice versa was recently shown to be not possible Cubitt, *et al.* [4] . As a consequence, we directly investigated the behavior and properties of suitable microscopic structure by means of microscopic molecular probes with the same dimensions. This will be shown step for step concerning well-established physical relations.

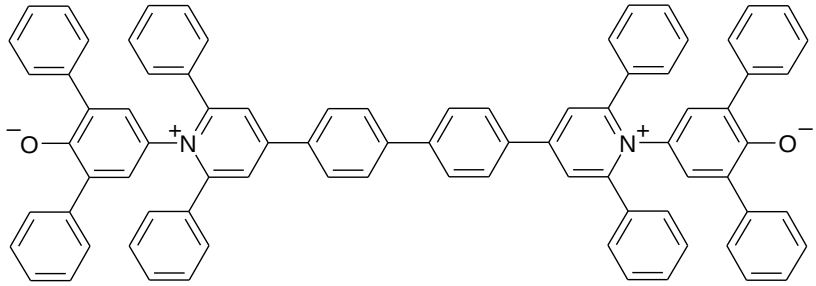
2. Materials and Methods

All optical materials were prepared according to the literature. The precise optical absorption and fluorescence measurements mainly rely on the perylenbiscarboximide chromophore such as the very soluble derivative **1**, briefly named perylene dye (S-13, CAS registry number RN 110590-84-6), because of their extraordinarily high lightfastness, chemical persistency and high fluorescence quantum yields close to unity [3, 5]; Figure-1. Thus, absorbed light will be stored within the fluorescence lifetime of some nanoseconds may be processed such as with energy transfer and can be efficiently and sensitively detected by means of florescence. The high chemical and thermal stability of the perylene dyes allow the construction of multichromophoric devices as optical functional materials.

Figure-1. The chemical structures of the perylene dye **1** (S-13) and the solvatochromic betaine dye **2**



1 **2**



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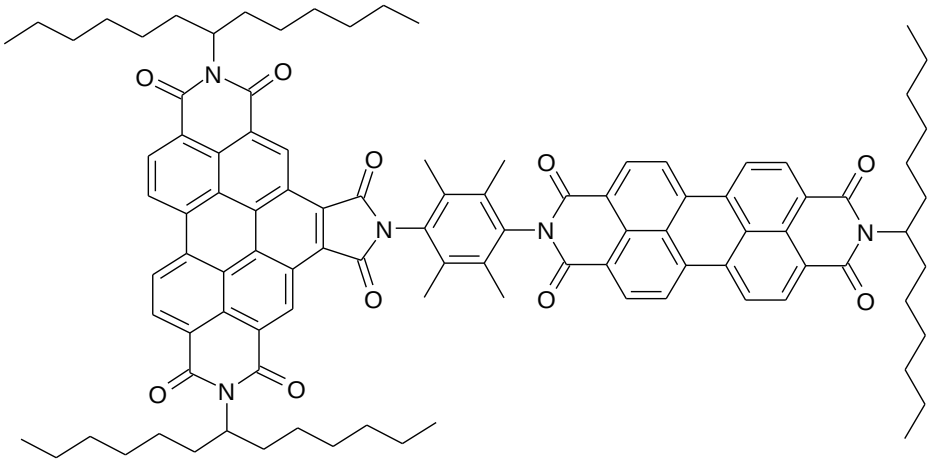

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Solvent effects were studied by means of the highly solvatochromic phenolate betaine **2** as an indicator for dipolarity [6] where medium-induced color changes were observed from the hypsochromic edge of the visible until the NIR. The molar energies of excitation of **2** known as $E_T(30)$ values in the literature [7] were taken as a measure for dipolarity and can be calculated for various solvents from the absorption maxima λ_{max} of **2** by means of equation (1). The $E_T(30)$ values were kept in kcal·mol^{-1} for compatibility with data bases in the literature and avoiding confusion; SI units may be obtained from $E_T(30)$ by multiplication with a factor 4.2.

$$E_T(30) = 28590 \text{ kcal·nm}/\lambda_{max} \quad (1)$$

The extension of the solvent shell was measured by means of the bichromophoreic dye **3** with antiparallel dipole moments [8] where the two sub-chromophores will operate independently for small solvent shell and compensate for extended solvent shells. Energy transfer of electronically excited states were measured by means of the bichromophore **4** where the left benzoperylene unit absorbes light at short wavelengthd and transfers energy to the right perylene chromopore emitting the energy of exitation as fluorescent light at longer wavelengths.

Measurements for UV/Vis absorption were performed in 1 cm quartz cuvettes with optical grade solvents where the absorptivities of the maxima were between 0.5 and 1.0 (spectrometer Varian Cary 5000). Fluorescence spectra were detected in 1 cm quartz cuvettes in 90° arrangement with optical densities of 0.01 until 0.025 (spectrometer Varian Eclipse) for routine measurements. Fluorescence lifetimes were determined with FluoTime300 of PicoQuant GmbH.

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3. Results and Discussion

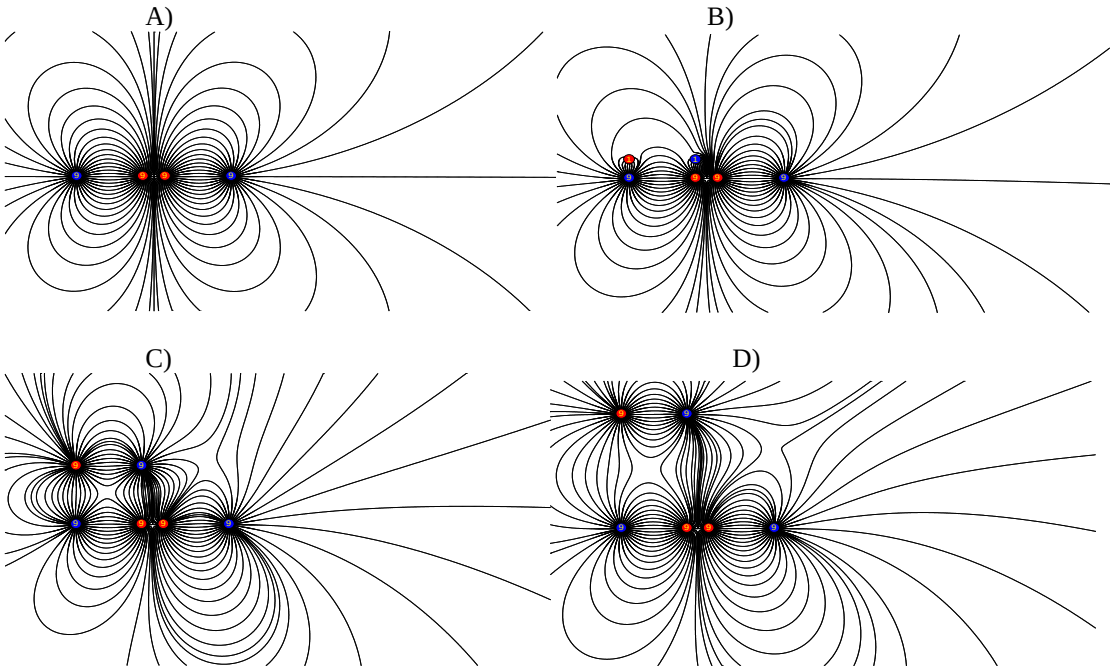
Molecular operating systems in the condensed phase should be considered more a microscopic unit with the incorporating medium such as a solvent or a macromolecular matrix than as isolated molecules because of their large surface with respect to the small volume. Strong interactions between the components can be expected even dominating the molecular properties [9]. Such interactions were globally treated as the solvent shell in the liquid phase; similar effects were observed for molecular structures in polymeric matrices [10]; compare also the effect of plasticizers. The extension of such solvent shells known as the first, second, third shell and so on is still under consideration; however, they may be important concerning the operating of individual molecular units and the function of molecular arrangements. The interaction of the water surface with the gas phase was investigated as a prototype of solvent effects. IR spectroscopic measurements gave the surprising result the only one layer of water molecules is responsible for the major effect of interaction [11]. Surfaces mean infinite two-dimensional perturbations of a liquid, whereas dissolved molecules mean small closed three-dimensional perturbations characterized as the solvent shell; this was determined with molecular probes.

3.1. Interaction with Non-Resonating Structures: Medium Effects and Solvent Shell

Light-absorbing molecular structures, dye molecules, were applied as probes for the measurements of solvent effects as non-resonating medium effects because of precise and efficient measurements. Molecules such as **2** with a permanent high dipole moment strongly interact with dipolar structures of media causing a lowering of the energy of the dye molecules [7]. The dipole moment of **2** will be appreciably diminished by the light-induced transition into the electronically excited state by intramolecular charge transfer; thus, the energetic stabilization of the electronic ground state by dipolar media whereas the electronically excited state is leaved essential unaffected will cause an increase of the transition energy meaning a shift of the light absorption to shorter wavelengths classified as a negative solvatochromism. The betaine **2** exhibits one of the strongest known solvatochromism where shifts from yellowish solutions in water, red in methanol violet in ethanol, blue in butanol, green in acetone and in the NIR absorbing in 1,4-dioxane were observed. The spectral shifts of **2** were applied as a useful highly sensitive molecular tool for the precise determination of the dipolarity of solvents and further interactions with the molecular neighborhood.

Two chromophores of **2** were arranged with anti collinear dipole moments in the molecular dyad **3** where compensating effects of the dipoles will be expected for large distances [8], however, individual dipolar interactions were expected for the nearest molecular proximity. This is visualized true to scale by the calculation [12] of electric streamlines in Figure-2 where A) means the streamlines of two anti-collinearly arranges dipoles. A third close dipole in B) essentially interacts with the left dipole. Increasing distances of the third dipole in C) and D) involves more and more also the right dipole where compensating effects of the anti-collinear arrangement become more and more important. Thus, compensating effects can be taken as a measure of the third dipole simulating the effects of solvating dipolar molecules.

Figure-2. Calculated streamlines [12]of anti-collinear arrangement of electric dipoles corresponding to a molecular size of 1300 pm for **3**.
A) Streamlines of undisturbed anti-collinear dipoles in the dimensions of **3**.
B) The left dipole interacts with a proximal third dipole, whereas the right remains essentially unaffected. C) and D): Third dipole more distant.

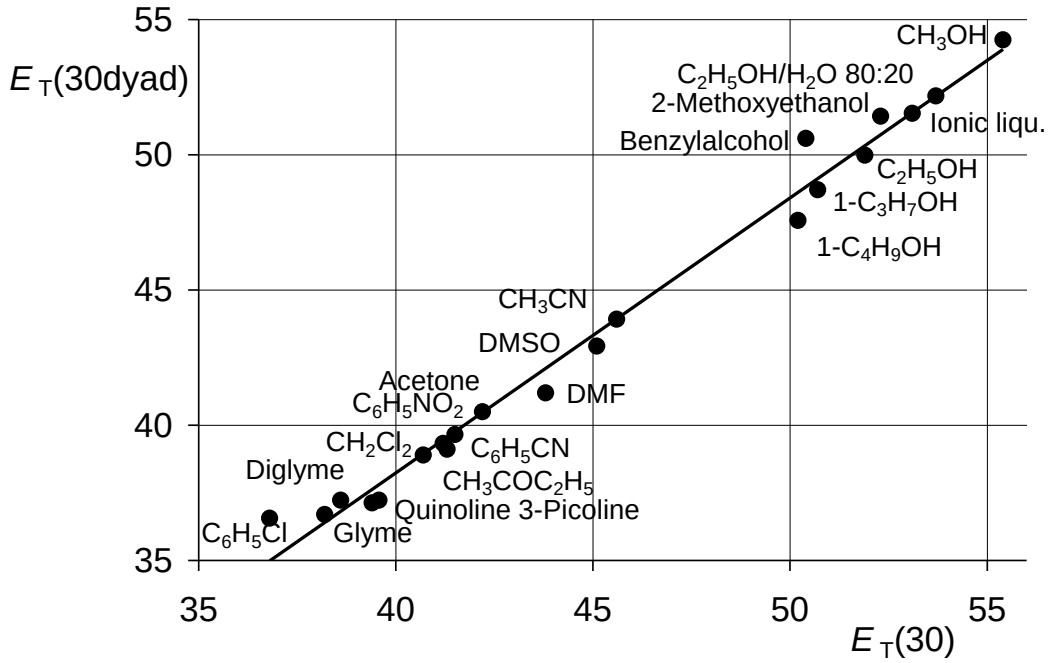


All dipolar interactions on the molecular level will be monitored by spectral shifts (λ_{max}) of the probes **2** and the bichromophoric (dyad) **3** transformed to the molar energies of excitation $E_T(30)$ by means of equation (1) for **2** and E_T(bic) with equation (2) for **3**.

$$E_T(30\text{dyad}) = 28590 \text{ kcal}\cdot\text{nm}/\lambda_{max} \qquad (2)$$

The molar energies of the excitation E_T(bic) of **3** were correlated with the $E_T(30)$ of **2** for various solvent with very different dipolarities; a linear correlation is expected [$E_T(30\text{dyad}) = a \cdot E_T(30) + b$ with the constants a and b] where the slope a is an indicator for compensating effects for **3** in that way that a slope of zero is expected for full compensation at infinite distant and a becoming larger for incomplete compensation ending up in unity for complete independent operation of both chromophores for a very tight solvent shell.

Figure-3. Solvatochromism of **3** [$E_T(30\text{dyad})$] for twenty pure solvents compared with the solvatochromism of **2** [$E_T(30)$] and their mutual linear correlation calculated by the least square method; slope: 1.02, intercept: 2.43, correlation number r: 0.993, for n = 20, standard deviation in $E_T(30\text{dyad})$: 0.7. Ionic liqu.: The ionic liquid is 1-butyl-3-methylimidazolium tetrafluoroborate.



The good linear correlation between the $E_T(30)$ and $E_T(30\text{dyad})$ values for various solvents is shown in Figure-3 where a slope very close to unity indicates the independent operation of both chromophores in **3**. As a consequence, the solvent shell must be very tight, not much more than one solvent molecule thick. Thus, the direct molecular surrounding may influence the operation of a molecular operating unit, whereas the more distant solvent remains unimportant.

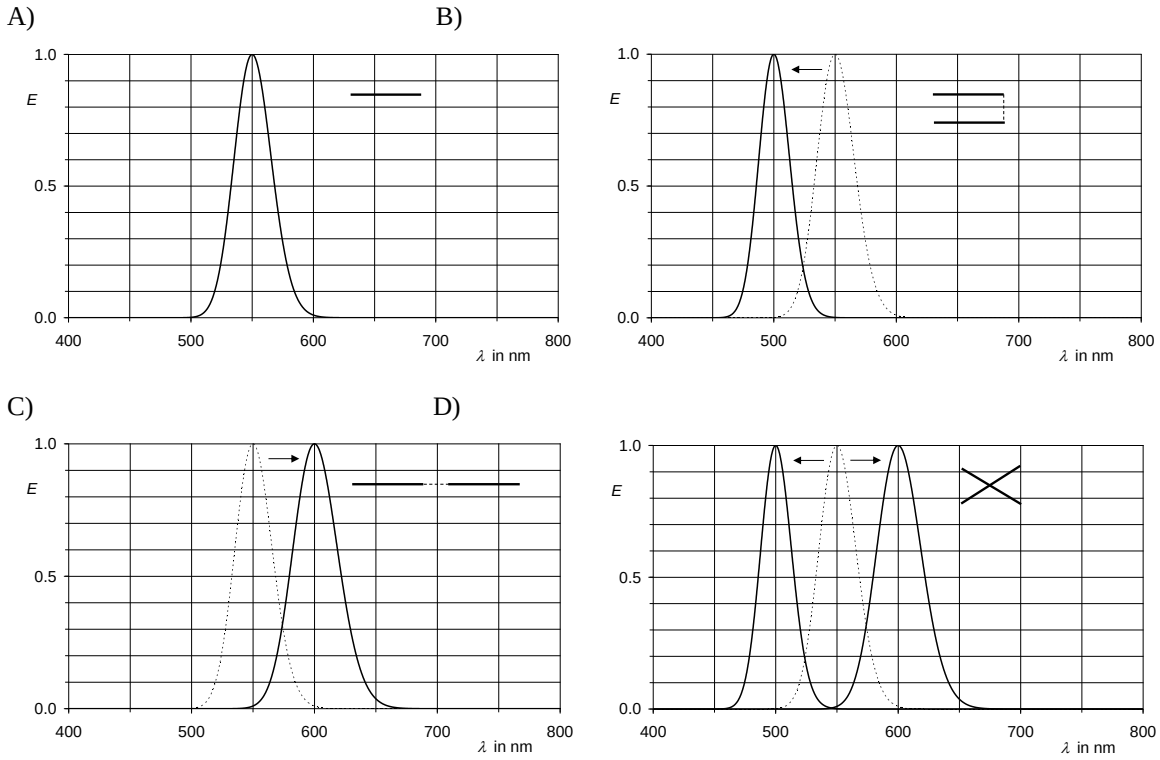
3.2. Interactions with Resonating Structures: Short Path Interactions

The interaction of chromophores with resonating molecular structures (structures with similar energetic eigenvalues) are completely different from the interactions with non-resonating solvent molecules. Energetic consequences of the direct contact or near neighborship of two or more chromophores (direct contact until distances of few lengths of the chromophore) were theoretically treated by Kuhn [13] and Davydov [14], experimentally investigated by Scheibe [15] and Jelley [16] and clearly expressed by Foerster [17]. One isolated dye molecule absorbs light energy with the transition energy E of the electronic ground state into an electronically excited state. The energy E of absorbed light quantum is interrelated with the wavelengths by Einstein's Formula (4) with Planck's constant h The frequency h the velocity of light c and the wavelengths λ.

$$E = h\cdot\nu = h\cdot c/\lambda \qquad (3)$$

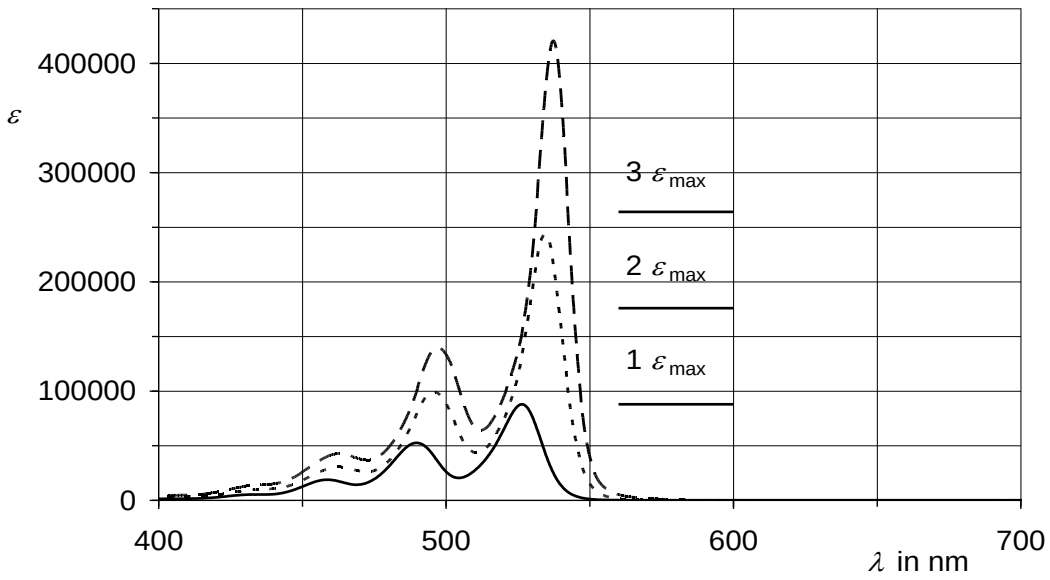
Bringing two identical molecules into interaction causes a shifting of the initially identical energies of the ground states so that states with a higher and a lower energetic level will be generated. The same effect proceeds with the electronically excited states. There are two electronic transitions allowed between these four different electronic levels because of quantum chemical selection rules. As a consequence, there are two transitions, one with longer and one with shorter wavelength instead the initial one of each chromophore; this effect is known as Davydov [18] splitting. The orientation of the electronic transition moments is responsible for the intensities of the transitions.

Figure-4. Simulated UV/Vis absorption as a Gaussian curve at 550 nm linear in energy and transition moment schematically indicated by a horizontal bar. B) Hypsochromically shifted UV/Vis spectrum (solid curve) compared with the initial spectrum (dotted curve) of two coplanar transition moments indicated by two parallel lines right. C) Bathochromically shifted UV/Vis spectrum (solid curve) compared with the initial spectrum (dotted curve) of two collinear transition moments indicated by two collinear lines right. B) Hypsochromically and bathochromically shifted UV/Vis spectra (solid curves) compared with the initial spectrum (dotted curve) of two skew-arranged transition moments indicated by two crossing lines right.



Some of the electronic transitions may be suppresses depending on the orientation of the transition moments; see Figure-4. A coplanar arrangement favors the hypsochromic transition (Figure 4-B), whereas the bathochromic is favored by a linear arrangement (Figure-4-C). Finally, a skew arrangement allows both transitions (Figure-4-D). Moreover, B shortens the effective lengths of the molecular antenna lowering the absorptivity ε so that less than two times the absorptivity of a single chromophore is observed. On the other hand, the effective lengths of the antenna in increased in C so that more than two times of the absorptivity of a single chromophore will be obtained [19]. This is clearly indicated in Figure-5 for linearly arranged perylene chromophores.

Figure-5. UV/Vis absorption spectra of linearly arranged perylene chromophores in chloroform solution. Solid curve dye **1**, Dotted curve: Two linearly arranged perylene chromophores interlinked at the nitrogen atoms. Dashed curve: Three linearly arranged perylene chromophores. The multiple ε values are indicated by bars demonstration the exceeding of ε by interactions becoming even more than four time of the individual value for three linearly arranged chromophores. (The molar absorptivity ε in $L \cdot mol^{-1} \cdot cm^{-1}$.)



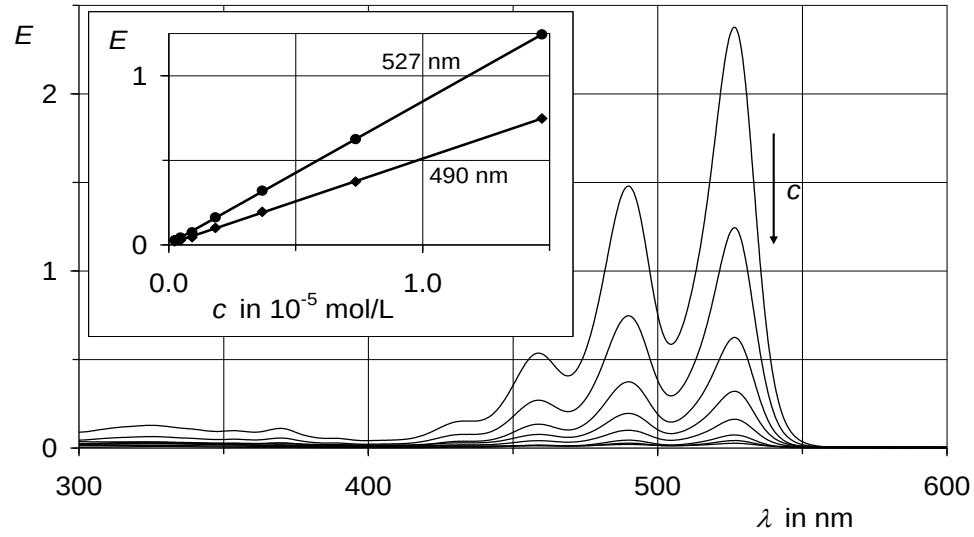
The effect of interactions between resonating chromophores as indicated by Figure-4 is comparably strong for a tight contact such as a linking by single bonds resulting in the spectra of Figure-5. There is a fast damping of the effect with an increasing separation of the chromophores becoming vanishing for distances in the order of the lengths of the chromophores themselves.

3.3. Interactions with Resonating Structures: Far-Reaching Interactions

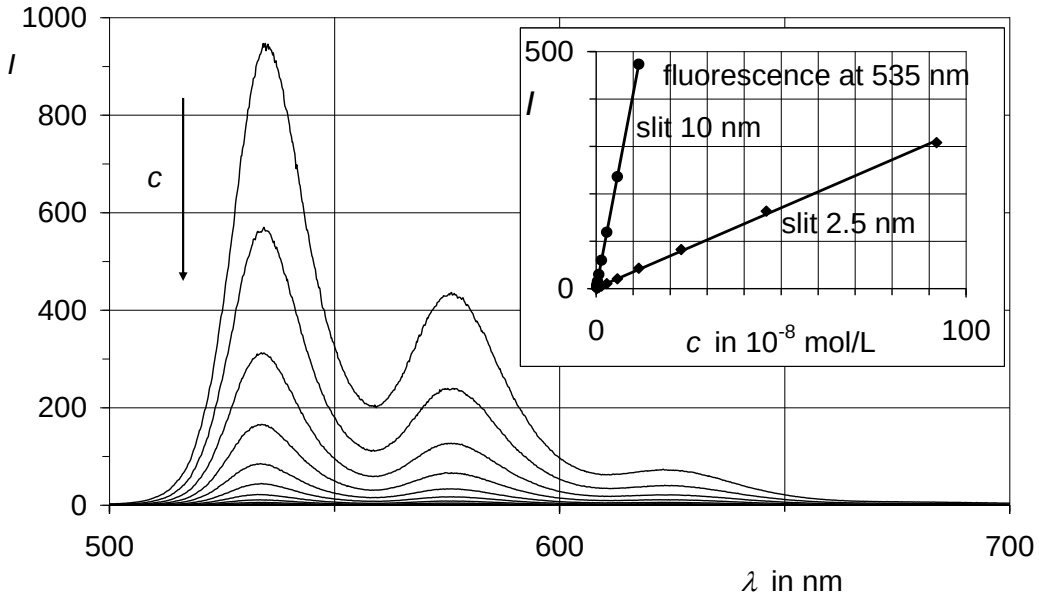
Dissolved dye molecules in diluted solutions of 10^{-4} molar or less are generally estimated to be independent from each others. The validity of Lambert Beer's law as the linearity between the absorptivity E and the concentration c of the dye is as well a good proof as the linearity of the intensity I of fluorescence and the concentration c; see Figure-6.

Figure-6: A) Upper diagram: UV/Vis absorption spectra of **1** in chloroform with propagating dilution. Insert: Precise verification of Lambert-Beer's law by the linear correlation of the absorptivity E as a function of the concentration c of **1**; circles: 527 nm, slope $0.810 \cdot 10^5$ L·mol^{-1}, standard deviation 0.49 %, correlation number 0.99995, coefficient of determination 0.9999, 7 measurements) and diamonds: 490 nm (slope $0.504 \cdot 10^5$ L·mol^{-1}, standard deviation 0.44 %, correlation number 0.99988, coefficient of determination 0.9998, 7 measurements). B) Lower diagram: Fluorescence spectra of **1** in chloroform with optical excitation at 489 nm and propagating dilution. Insert: Linear correlation of the intensity I of fluorescence as a function of the concentration c of **1**; diamonds: Slit for excitation 2.5 nm (slope $3.38 \cdot 10^8$ L·mol^{-1}, standard deviation 3.1, correlation number 0.9995, coefficient of determination 0.9991, 11 measurements) and steep line, circles: Slit for excitation 10 nm (slope $4.11 \cdot 10^9$ L·mol^{-1}, standard deviation 0.33, correlation number 0.999998, coefficient of determination 0.999997, 8 measurements).

A)



B)



Moreover, the shapes of both absorption and fluorescence spectra remain unaltered with propagating dilution; see Figure-6. As a consequence, UV/Vis absorption and fluorescence spectra and fluorescence quantum yields

remain independent from the concentration for 10^{-4} molar and further diluted solutions indicating isolated dye molecules.

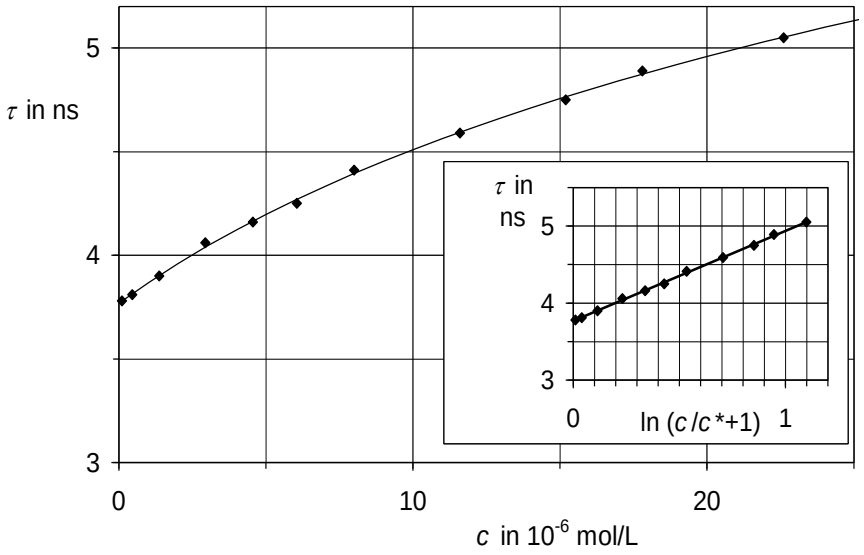
$$\frac{1}{\tau_0} = A_{u\to l} = 1000\frac{8\pi \ln(10) c \tilde{\nu}_{u\to l}^2 n^2}{N_A}\frac{g_l}{g_u}\int \varepsilon d\tilde{\nu} \qquad (4)$$

$$\frac{1}{\tau_0} = \frac{2.880\cdot 10^{-9}}{\mathrm{cm}\cdot\mathrm{s}} n^2 \tilde{\nu}_0^2 \frac{g_l}{g_u}\int \varepsilon d\tilde{\nu} \qquad (5)$$

$$\tau = \phi \cdot \tau_0 \qquad (6)$$

The theoretically derived [20] and widely applied Stickler-Berg equation (4) interrelates the fluorescence quantum yield Φ with the fluorescence lifetime τ. N_A means Avogadro's constant $\tilde{\nu}_{l\to u}$ the wavenumber of the electronic transition lower *l* to upper *u*, *c* the velocity of light, *n* the index of refraction and g_l and g_u the degeneracies of the lower and the upper energetic state, respectively. There are some mathematical constants, the factor 1000 for the adaption to SI units and the integral extending over the absorption band, thus representing the oscillator strengths. The ratio of the degeneracies becomes unity for most complex organic chromophores because of low symmetry. The factors can be combined to the constant in equation (5) with $\tilde{\nu}_0$ being the mean wavenumber of the absorption band. The molar absorptivities of the maxima are proportional to the oscillator strengths for identical shapes of UV/Vis spectra. Equation (4) was established for strongly light-absorbing dyes ($\varepsilon \geq 8000$) with small geometrical distortion upon light absorption indicated by small Stokes' shifts. The natural lifetime τ_0 can be interrelated with the apparent lifetime τ and the fluorescence quantum yield ϕ by means of equation (6).

Figure-7. Dependence of the fluorescence lifetime τ of **1** in chloroform on the concentration *c* (diamonds; see Table 1). Curve: Function $a\cdot\ln(c/c^* + 1) + \tau_\infty$ according to equation (8) with a = 1.17 ns, c^* = $1.17\cdot10^{-5}$ mol·L^{-1} and τ_∞ = 3.77 ns. Insert: Linear correlation according to equation (7) (standard deviation 0.015, correlation number 0.9992, coefficient of determination 0.9984, 11 measurements).



Equation (4) refers only to molecular and atomic properties, respectively, and the fluorescence lifetime τ should be thus independent of the concentration of the fluorescent dye in diluted solutions [21].; this was generally accepted in the literature. This postulated independency was re-examined by means of dye **1** because of its high fluorescence quantum yield of close to unity [22] simplified equation (6) and excludes interference caused by variation of the fluorescence quantum yield because the latter is close to unity for diluted solutions and remains close to unity upon further dilution. Surprisingly, a comparably strong dependence of the lifetime τ of the concentration of **1** is observed [23] in contrast to the theory; see Figure-7 and Table-1.

Table-1. Fluorescence lifetimes τ of **1** in chloroform depending on the concentration *c* and the mean molecular distance *d*, respectively. Fluorescence excitation at 490 nm and detection at 535 nm.

c 10^{-6} **mol·L^{-1}** [a]	τ **ns**[b]	***l*** **nm**[c]	***d*** **nm**[d]
22.6	5.04	42	23
17.8	4.91	45	25
15.2	4.77	48	26
11.6	4.59	52	29
8.00	4.41	59	33
6.05	4.29	65	36
4.56	4.13	71	40
2.94	4.05	83	46
1.37	3.90	106	59
0.456	3.82	154	85
0.108	3.79	249	138

[a] Molar concentration of dye **1** in chloroform. [b] Time constant τ for the exponential decay of fluorescence. [c] Calculated lengths of the cubic volume for one dye molecule [d] Calculated mean inter molecular distance [24] for **1**.

The variation of τ can be seen in relation of the dimension of the length *l* of a standard cube for one molecule or by the mean molecular distance *d* calculated according to Chandrasekhar's method [24]; see Table 1. Here we can see that interactions become important until a distance of ore than one tenth of the wavelength of fluorescence light and reach macroscopic dimensions. As a consequence, the light emission by fluorescence from electronically excited molecules resembles less a quantum chemical process, but more the radiation of radio waves from a complex arrangement of active and passive resonators such as popular by the Yagi-Uda antenna [25]. On the other hand, completely novel technological possibilities are given by such far-reaching interactions such as macroscopic addressing of molecular structures [26].

$$d\tau/dc = a/(c + c^*) \qquad (7)$$

On can rationalise the changing of τ with the concentration *c* by means of the differential equation (7) where there firstly a constant change of the lifetime τ with the concentration *c* is assumed ($d\tau/dc$ = const.), however, the other chromophors also interact with each others decreasing inversely the at low concentrations constant change. With exceeding a certain concentration *c** this lowering becomes important so that the correction by *c* in the denominator on the right side of equation (7) becomes necessary; *a* and *c** are material-dependent constants.

$$\tau = a \cdot \ln\left(\frac{c}{c^*} + 1\right) + \tau_\infty \qquad (8)$$

The integration of equation (7) results in equation (8) with the dimensionless logarithmic expression where τ_∞ means the fluorescence lifetime at infinite dilution. Equation (8) describes the concentration dependence of the fluorescence lifetime quite precisely as one can see from the curve in Figure (7) and the linear correlation shown in the insert. Equation (8) is useful for practical application for interpolation and general planning.

3.4. Dipole Dipole Interactions with Neighboring Chromophores: Resonance Energy Transfer

Energy transfer is important for optical molecular data processing. A gradient in energy is necessary for a directed transport and can be realized by the combination of different chromophores absorbing at shorter (higher energy of excitation, hypsochromically) and longer wavelengths (lower energy of excitation, bathochromically). The energy of excitation can be transferred from hypsochromically absorbing donors to bathochromically absorbing chromophores as the acceptors. However, the energy of light will not be a continuous stream, but more individual

light quanta. Thus, one has to concern about the mechanism of the energy transfer between molecular structures of donors and acceptors. Förster favored the now widely accepted mechanism of transfer by resonant dipole dipole interaction [17, 27, 28] having become popular as FRET (*F*örster *r*esonant *e*nergy *t*ransfer) and developed equation (9) for the quantitative description of the process. There are some mathematical constants in equation (9), the factor 1000 for the adaption to SI units and Avogadro's number N_A, some spectroscopic data of the involved chromophores where J_{DA} means the integral of the spectral overlap between the fluorescence spectrum of the energy donor and the absorption spectrum of the acceptor, Φ_D the fluorescence quantum yield and τ_D the fluorescence lifetime of the donor. Important for the construction of molecular interacting optical units is the orientation factor κ for the rate constant k_{FRET} for the energy transfer and the dependence on the inverse 6th power of the distance $\boldsymbol{R}$ between the two chromophores causing a very fast damping. The latter is applied as a molecular ruler for many applications, however, for more recent discussions see Nalbach, *et al.* [29].

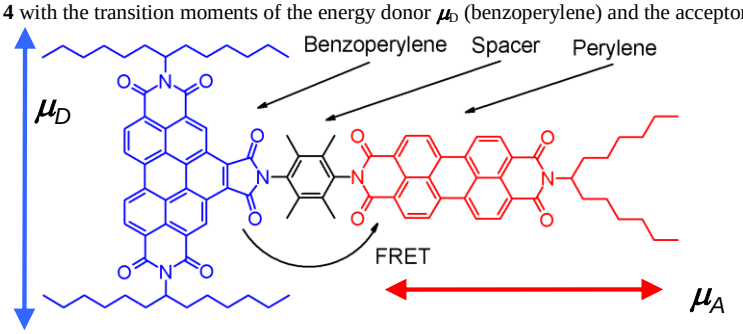
$$k_{FRET} = \frac{1000 \cdot (\ln 10) \cdot \kappa^2 \cdot J_{DA} \cdot \Phi_D}{128 \cdot \pi^5 \cdot N_A \cdot \tau_D \cdot \left|\boldsymbol{R}_{DA}\right|^6} \quad (9)$$

The orientation factor κ can be calculated from three scalar products. These can be simplified to equation (10) where θ_{DA} means the angle between the transition moment of the Donor D (μ_D) and the acceptor A (μ_A).

$$\kappa = \cos(\theta_{DA}) - 3 \cdot (\cos(\theta_D) \cdot \cos(\theta_A)) \quad (10)$$

θ_D means the angle between the transition moment of the donor and the vector between the donor and acceptor and θ_A is the corresponding angle concerning the acceptor. The applicability of equation (9) was tested with dyad **4** where the left benoperylene chromophore is hypsochromically light-absorbing with a transition moment parallel to the connection between the two nitrogen atoms of the six-membered rings and the right bathochromically absorbing with an orthogonal transition moment along the long molecular axis; see Figure 8.

Figure-8. The dyad **4** with the transition moments of the energy donor μ_D (benzoperylene) and the acceptor μ_A (perylene).

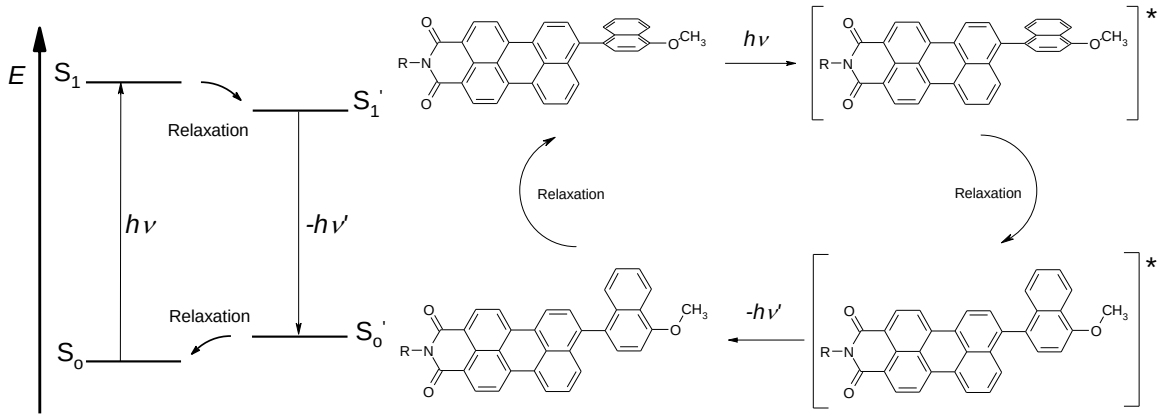


Thus, the orientation factor κ is expected to become zero for **4** because both θ_{DA} and θ_D become 90° and both terms in equation (10) become zero. As a consequence, a suppression of FRET is expected with independent operation of both chromophores. In contrast to this theoretical prediction, a very fast and efficient energy transfer (close to 100%) from the donor to the acceptor is observed with a time constant of only 9.4 ps [30]; intramolecular motions may be therefore responsible. As a consequence, the dipole dipole concept of the energy transfer according to equation (9) cannot be applied to real molecular systems. This interfers with possibilities of intramolecular optical isolation by means of the orientation of chromophores. On the other hand, there are no geometrical restrictions for inter molecular energy transfer processes.

3.5. Dynamic Processes

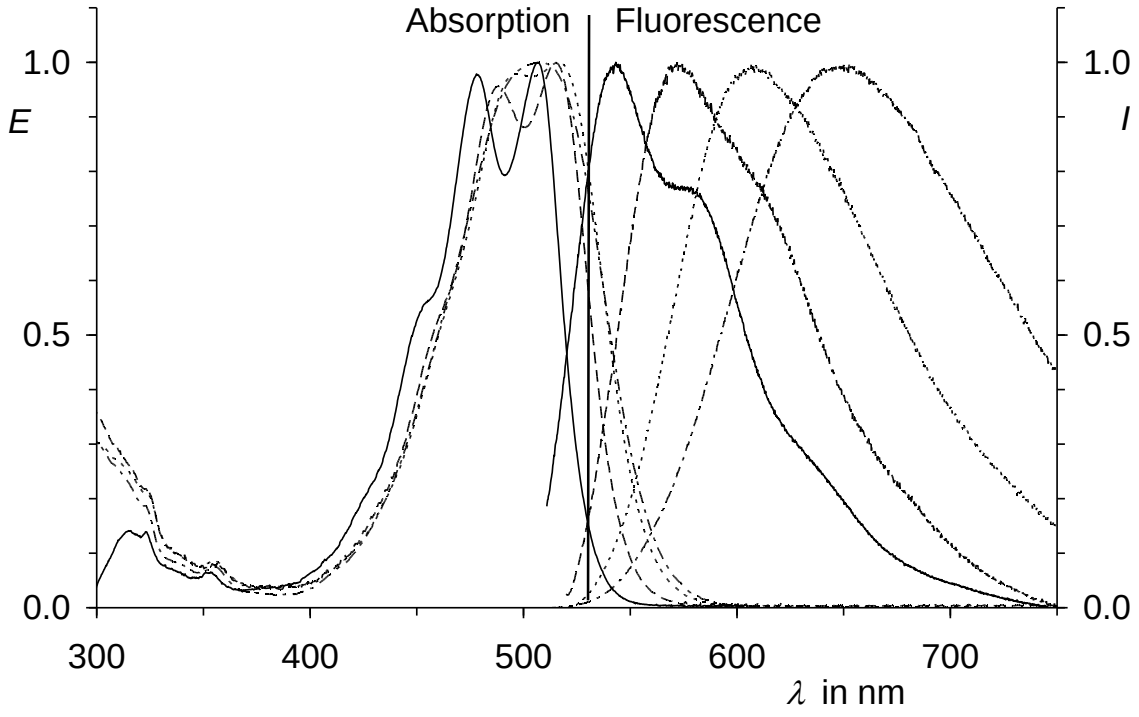
Fluorescent dyes are able to re-emit absorbed light with mostly an exponential decay of intensity. The fluorescence lifetime (time constant of the exponential) of the majority of highly fluorescent chromophores is in the order of some ns such as for **1** with about 4 ns. The energy of light is stored during this short period by the chromophore and may be processed; without processing, such as with the stiff and firm **1**, re-emission proceeds at about the same wavelength as absorption, classified as a small Stokes' shift between the maximum of absorption and fluorescence. Flexible molecular structures are suitable for a passive processing the energy of absorption by means of relaxation processes [31] according to Figure 9.

Figure 9. Relaxation processes in fluorescent dyes increasing the Stokes' shift. Left: Schematic absorption of light ($h\nu$) from the ground state S_o to the first electronically excited state S_1 and subsequent relaxation to S_1', bathochromically shifted light emission ($h\nu'$) and relaxation to the initial state S_o. Right: Perylene carboximide with attached methoxynaphthalene and relaxation processes by torsion of an inter-linking single bond.



Torsion of a inter-linking single bond between two aromatic systems allows angle-dependent an electronic coupling or decoupling of two aromatic systems. Such a relaxation process allowed the construction of fluorescent dyes with increased Stokes' shift because the relaxation process proceeds with the lowering of the energy of excitation and thus, causes a bathochromic shift of the emission. Such relaxation processes can be combined with the solvent effects allowing the tuning of the Stokes' shift by means of the medium. This was shown [32] with the methoxynaphthalene-perylene carboximid in Figure 9 right where there is an electron donor (OCH_3 group) conjugated with an acceptor group (carbonyl group of the carboximide) establishing a dipole moment making the electronic transition sensitive to solvent influence. This is moderate in the electronic ground state, however, becomes large in the electronic excite state (S_1). As a consequence, UV/Vis absorption is moderate solvatochromic, whereas fluorescence becomes highly solvatochromic where the wavelengths of fluorescence and the energy of electronic excitation for further processing such as energy transfer, respectively, can be tuned by means of the dipolarity of the medium.

Figure 10. Solvatochromism of naphthalene-perylenebiscarboximide according to Figure 9; maxima from left to right: Solvents *n*-heptane (solid curves), toluene (dashed curves), chloroform (dotted curves) and ethanol (dotted dashed curves). Left side: Weak sovatochromism in light absorption; right side strong solvatochromism in fluorescence.



A twisting around the interlinking single bond in the electronic ground state seems to be an essential prerequisite for a relaxation according to Figure 9. A joint increase of the dipole moment means formally an intramolecular charge transfer from the donor to the acceptor; thus, such electronic excitations were classified [33] as TICT states (twisted intra molecular charge transfer). The prerequisites for such processes were studied with the similar *peri*-arylnaphthalenecarboximides [34] indicating the favoring effect of a twisting; however, a firm, stiff and complete orthogonal arrangement quenches fluorescence. As a consequence molecular geometry has to be properly balanced for optimal operating.

3.6. Light-Driven Electron Transfer (PET)

An interlink between molecular and conventional electronics is given by light-driven charge transfer processes both for interfaces between the two types of electronics and technologies such as in solar cells. Electron rich and electron depleted chromophores were interconnected for charge separation such as with corroles and perylene biscarboximides [35]. The charge separation was successful in such dyads; however, an adaptation to special requirements remains difficult because not only two chromophores have to be simultaneously adapted, but also their electron richness. Better prerequisites are given by a combination of one chromophore to be tuned to the requirements and a local electron rich structure such as generated be α-effect donor groups consisting of two directly conneted atoms with lone electron pairs where a charge separation until 1.6 nm was successful [36].

4. Conclusion

Concepts from macroscopic electronics can be applied for microscopic electronics in many cases. Optical technologies are attractive for microscopic, molecular IT devices because of both the high frequencies at 0.5 PHz and the still unproblematic handling of radiation where chromophores will be the operating components. The quantization of light emission and absorption causes major differences and special necessities compared with macroscopic electronics. Chromophores generally contain polar groups and strongly interact with media where the dipolarity becomes important. On the other hand, the thus caused solvent shell is very small and can be treated as a unit with the chromophore. A direct contact of chromophores until a distance of about 1 nm causes electronic coupling with a splitting of the energetic levels where one or both levels may be active and controlled by molecular orientation. The over all orientation is also responsible for an amplification or declining of the absorptivity of the system. The interactions of chromophores until about 5 nm can be described by dipolar processes and are responsible for resonant energy transfer where the well-established concept of FRET has to be modified because of discrepancies both concerning the distance function and the orientation of transition moments. A novel type of interaction between chromophores was found until distances of more than 150 nm by means of the concentration dependence of the fluorescence lifetime. This resembles more the near field of a radio transmitter than an quantum physical system and basically offers possibilities for a macroscopic electronic addressing of microscopic molecular structures. A further interface between conventional electronics and molecular structures can be established by light-driven electron transfer and charge separation where solar cells are one of the most popular applications. Finally, many concepts of macroscopic electronics can be kept in the molecular level, however quantization and some new findings have to be considered; as a consequence, a combination of both will be a good concept to the next generation of IT devices.

References

[1] Hilbert, M. and López, P., 2011. "The world's technological capacity to store, communicate, and compute information." *Science*, vol. 332, pp. 60-65.

[2] Carroll, R. L. and Gorman, C. B., 2002. "The genesis of molecular electronics." *Angew. Chem. Int. Ed.*, vol. 41, pp. 4378-4400.

[3] Langhals, H., 2014. "Handling electromagnetic radiation beyond terahertz using chromophores to transition from visible light to petahertz technology." *J. Electr. Electron. Systems*, vol. 3, p. 125.

[4] Cubitt, T. S., Perez-Garcia, D., and Wolf, M. M., 2015. "Undecidability of the spectral gap." *Nature*, vol. 528, pp. 207–211.

[5] Langhals, H., 2013. *Chromophores for picoscale optical computers. In Sattler, K. (ed.), Fundamentals of picoscience*. Bosa Roca/US: Taylor & Francis Inc. CRC Press Inc. pp. 705-727.

[6] Dimroth, K., Reichardt, C., Siepmann, T., and Bohlmann, F., 1963. "Über pyridinium-n-phenol-betaine und ihre verwendung zur charakterisierung der polarität von lösungsmitteln." *Justus Liebigs Ann. Chem.*, vol. 661, pp. 1-37.

[7] Reichardt, C. and Welton, T., 2011. *Solvents and solvent effects in organic chemistry*. 4th ed. Wiley-VCH: Weinheim.

[8] Langhals, H., Braun, P., Dietl, C., and Mayer, P., 2013a. "How many molecular layers of polar solvent molecules control chemistry? The concept of compensating dipoles." *Chem. Eur. J.*, vol. 19, pp. 13511-13521.

[9] Langhals, H., 2017a. "Heterocyclic structures applied as efficient molecular probes for the investigation of chemically important interactions in the liquid phase." *Chem. Heterocycl. Compd.*, vol. 53, pp. 2-10.

[10] Langhals, H., 1982. "Polarity of organic glasses." *Angew. Chem.*, vol. 94, pp. 452-453.

[11] Stiopkin, I. V., Weeraman, C., Pieniazek, P. A., Shalhout, F. Y., Skinner, J. L., and Benderskii, A., 2011. "Hydrogen bonding at the water surface revealed by isotopic dilution spectroscopy." *Nature,* , vol. 474, pp. 192-195.
[12] Stöckl, J., 2007. "Electric fields." Available: http://www.crazybytes.at/didact/didact_simul_D.htm#Elfeld
[13] Kuhn, W., 1930. "The physical significance of optical rotatory power." *Trans. Faraday Soc.*, vol. 26, pp. 293-308.
[14] Davydov, A. S., 1948. "Theory of absorption spectra of molecular crystals." *Zhur. Eksptl. i Teoret. Fiz., 18: 210-218; Chem. Abstr.*, vol. 43, p. 4575f.
[15] Scheibe, G., 1936. "Variability of the absorption spectra of some sensitizing dyes and its cause." *Angew. Chem.*, vol. 49, p. 563.
[16] Jelley, E. E., 1936. "Spectral absorption and fluorescence of dyes in the molecular state." *Nature,* , vol. 138, pp. 1009-1010.
[17] Foerster, T., 1946. "Energy transport and fluorescence." *Naturwiss*, vol. 33, pp. 166-175.
[18] Davydov, A. S., 1962. *Theory of Molecular Excitations. Trans. H. Kasha and M. Oppenheimer, Jr.* New York: McGraw-Hill.
[19] Langhals, H. and Jona, W., 1998. "Intense dyes through chromophore-chromophore interactions: Bi- and trichromophoric perylene-3,4:9,10-bis(dicarboximide)s." *Angew. Chem*, vol. 110, pp. 998-1001.
[20] Strickler, S. J. and Berg, R. A., 1962. "Relationship between absorption intensity and fluorescence lifetime of molecules." *J. Chem, Phys.*, vol. 37, pp. 814-822.
[21] Jose, J. and Burgess, K., 2006. "Benzophenoxazine-based fluorescent dyes for labeling biomolecules." *Tetrahedron*, vol. 62, pp. 11021–11037.
[22] Langhals, H., Karolin, J., and Johansson, L. B.-Å., 1998a. "Spectroscopic properties of new and convenient standards for measuring fluorescence quantum yields." *J. Chem. Soc., Faraday Trans.*, vol. 94, pp. 2919-2922.
[23] Langhals, H. and Schlücker, T., 2014a. "The use of dilute chromophore fluorescence decay time for concentration determination. Ger. Offen. DE 102014006209.0 (April 29, 2014)." *Chem. Abstr.*, vol. 163, p. 714018.
[24] Chandrasekhar, S., 1943. "Stochastic problems in physics and astronomy." *Rev. Mod. Phys.*, vol. 15, pp. 1-89.
[25] Yagi, H., 1928. "Beam transmission of ultra short waves." *Proc. of the IRE*, vol. 16, pp. 715-740.
[26] Langhals, H., 2017. "A concept for molecular addressing by means of far-reaching electromagnetic interactions in the visible." *J. Electr. & Electron. Systems*, vol. 6, p. 125.
[27] Foerster, T., 1948. "Intermolecular energy transfer and fluorescence." *Ann Phys 6. Folge*, vol. 2, pp. 55-75.
[28] Foerster, T., 1949. "Experiments on intermolecular transition of electron excitation energy." *Z Elektrochem*, vol. 53, pp. 93-99.
[29] Nalbach, P., Pugliesi, I., Langhals, H., and Thorwart, M., 2012. "Noise-induced Förster resonant energy transfer between orthogonal dipoles." *Physical Review. Lett.*, vol. 108, pp. 218302-1 - 218302-5.
[30] Langhals, H., Esterbauer, A. J., Walter, A., Riedle, E., and Pugliesi, I., 2010. "Förster resonant energy transfer in orthogonally arranged chromophores." *J. Am. Chem. Soc.*, vol. 132, pp. 16777-16782.
[31] Langhals, H. and Hofer, A., 2012. "Controlling UV/Vis absorption and Stokes' shifts in highly fluorescent chromophores by molecular dynamics in targeted construction of dyads." *J. Org. Chem.*, vol. 77, p. 585−9592.
[32] Greiner, R., Schlücker, T., and Langhals, H., 2017. "Quasi TICT state driven molecular photo-flipping medium-controlled light emitters." *In preparation*,
[33] Rettig, W., 1986. "Charge separation in excited states of decoupled systems: twisted intramolecular charge transfer (TICT) compounds and implications for the development of new laser dyes and for the primary process of vision and photosynthesis." *Angew. Chem.*, vol. 98, pp. 969-986.
[34] Greiner, R., Schlücker, T., Zgela, D., and Langhals, H., 2016. "Fluorescent aryl naphthalene dicarboximides with large Stokes' shifts and strong solvatochromism controlled by dynamics and molecular geometry." *J. Mater. Chem. C*, vol. 4, pp. 11244-11252.
[35] Flamigni, L., Ciuciu, A. I., Langhals, H., Böck, B., and Gryko, D. T., 2012. "Improving the photoinduced charge separation parameters in corrole-perylene carboximide dyads by tuning the redox and spectroscopic properties of the components." *Chem. an Asian J.*, vol. 7, pp. 582-592.
[36] Langhals, H., Obermeier, A., Floredo, Y., Zanelli, A., and Flamigni, L., 2009. "Light-driven charge separation in isoxazolidine-perylene bisimide dyads." *Chem. Eur. J.*, vol. 15, pp. 12733-12744.